

A High Conduction Composite Li Superionic Conductor

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Energy storage plays a pivotal role in the next generation portable electronic devices and electrified transportation. Under such scenario, there is an increasing need for high energy density storage devices. The current generation Li-ion batteries need significant improvements to satisfy such a need.

Lithium batteries with elemental electrodes (Metallic Li Anode and S/O₂ Cathode) offer significant improvement in theoretical specific energy. Issues with formation of reversible Li₂O₂ and electrolyte stability have prevented the development of Li-O₂ batteries. Li-S batteries offer a 6 fold increase in theoretical specific energy over the conventional Li-ion cells (2,567 Wh kg⁻¹ vs 387 Wh kg⁻¹)¹. However, these cells suffer from the dendritic growth on Li anodes and polysulfide shuttle phenomenon that arises from the use of liquid electrolytes^{1,2}. Solid state electrolytes offer a simple solution to these issues via their electrochemical, mechanical and thermal stability. Despite these advantages, a majority of the solid state electrolytes suffer from poor ionic conductivity and instability vs. metallic Li anodes³. Two solid state Li-ion conductors that possess good Li-ion conductivity and stability against Li anode are the cubic Li₇La₃Zr₂O₁₂ (LLZO)⁴ and β-Li₃PS₄ (LPS)⁵. While they offer a solution for Li batteries, the interfacial conductivity of LLZO with electrodes and high temperature materials processing needs to be addressed⁶. Similarly the room temperature conductivity of LPS can be improved for a much improved performance.

In this work, we address the aforementioned challenges through a composite of LLZO and LPS with a core-shell structure. The synthesis of LLZO and LPS was conducted using previously reported techniques by Rangasamy et. al.⁴ and Liu et. al.⁵ The core-shell structure was obtained through a simple dry coating procedure as illustrated in Figure 1. LLZO is a hard oxide and LPS is a soft sulfide. These complementary mechanical properties are essential to the formation of a homogenous core-shell structure that was confirmed by TEM analysis. These two electrolytes are chemically stable with one another. The physical contact of these two phases creates a space-charge layer at the interface between the sulfide and oxide. The space charge layer results in an ionic conductivity of the composite higher than its parent electrolytes. The effects of the space charge layer are more pronounced in the lower conducting weight fractions where impedance spectroscopy resolves the contributions from the space charge layer. The composite takes advantage of the merits of the two parent electrolytes while leaving out their respective demerits. The incorporation of hard LLZO is expected to improve the mechanical strength of LPS, while the high-temperature processing is not needed with the soft LPS that can be cold-pressed. In addition, the composite has a much lower interfacial resistance with metallic lithium compared to that of the hot-pressed LLZO. Systematic investigation of the LLZO-LPS composites was conducted with nano-crystalline and crystalline LPS, and

tetragonal and cubic forms of LLZO. The details of structural characterization and electrochemical performance of the composite electrolyte system will be presented at the meeting.

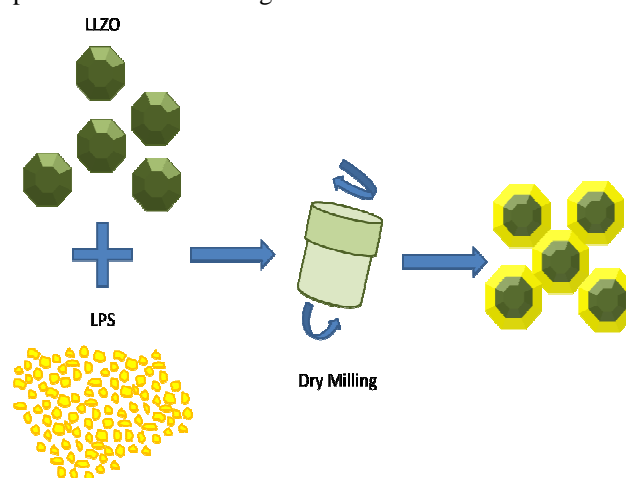


Figure 1. A core-shell structured LLZO-LPS composite via dry milling.

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